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Techniques are described for the determination of 1,2-Diols by indirect atomic absorption with digested lead periodate. Preliminary experiments indicate that styrene glycol can be determined in the presence of styrene epoxide. This is of particular interest because epoxide hydrase catalyzes the hydrolysis of an epoxide to a 1,2-diol. The procedure may lend itself to the determination of the enzyme activity of epoxide hydrase, known for its pivotal role in the metabolism of many carcinogens and toxic compounds.

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Determination of 1,2–Diols by Indirect Atomic Absorption with Digested Lead Periodate

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Oxidation with the periodate ion causing the specific 1,2-diol scission is the most useful tool in carbohydrate chemistry, as well as in the determination of this functional group. Frequently, the methods of analysis involve the determination of periodate consumed or the products formed, namely, formaldehyde, formic acid, or carbon dioxide (*1*, *2*).

The periodate ion absorbs at 222.5 nm and the decrease in absorbance has been used to quantify the amount of adjacent dihydric phenols (*3*, *4*). Colorimetric procedures, using the dinitrophenylhydrazine for the assay of glyceric acids and related compounds (*5*, *6*) and glycols (*7*) have also been reported.

Recently, indirect atomic absorption methods were employed for the determination of aliphatic secondary amines, aldehydes, and thiols (*8–10*). In each of these indirect atomic absorption spectrophotometry (IAAS) methods, a metallic precipitate formed with the analyte or with the product was incorporated in the final procedure before filtration and finally digested for analysis.

IAAS has been applied in the determination of 1,2-diols by Oles and Siggia (*11*). Periodic acid was used to oxidize the glycols. The iodate formed was then precipitated carefully as the silver iodate, filtered, rinsed, and digested before analysis for the silver content. The acid and reagent concentrations used, as well as the cooling of the preflocculated $AgIO_3$ to −10 to −15 °C were altogether critical for the preferential precipitation of $AgIO_3$ while keeping the periodate in solution. Determination of six samples by this procedure may be accomplished in 90 min.

In the present work, 1,2-diols were reacted with an excess potassium periodate, the remaining periodate was precipitated with excess lead nitrate and the lead periodate formed was separated from the reaction medium by membrane filtration. The precipitate was then dissolved in 1 M HNO_3 and analyzed for the lead content by atomic absorption spectrophotometry. Lead nitrate was used to prepare all calibration solutions and only one calibration curve was needed.

EXPERIMENTAL

Apparatus. A Perkin-Elmer 103 atomic absorption spectrophotometer was used. The 283.3-nm line from a single element (Pb) hollow cathode lamp, operating at a modulated half-wave current of 5.5 mA was used. The flame and slit setting were air–acetylene and 0.7 nm, respectively. Details of instrument settings may be obtained in Reference 12. All filtrations were accomplished with Nalgene (Nalge Co.) disposable filtration units (0.2-μm porosity). Each filter was repeatedly used for about 6 samples before discarding.

Reagents. Lead nitrate, 1,2-ethanediol, 1,2-propanediol, and 1,2,3-propanetriol (glycerol) were obtained from Fisher Scientific Co., while 1-phenyl-1,2-ethanediol (styrene glycol), 1-amino-2,3-propanediol, and 1,3,5-trihydroxybenzene (phloroglucinol) were obtained from Aldrich Chemical Co. 1,4-Dihydroxybenzene (hydroquinone) and 1,3-dihydroxybenzene (resorcinol) were purchased from MCB Manufacturing Chemists while 1,2-dihydroxybenzene (catechol) and 1,2,3-trihydroxybenzene (pyrogallol) were purchased from J. T. Baker Chemical Co. Finally, DL-β-3,4-dihydroxyphenylalanine (DOPA) and potassium periodate (or metaperiodate) were obtained from Sigma Chemical Co., and Baker and Adamson Co., respectively. The best available grades of these compounds were used without further purification. All diols were prepared in aqueous solution and kept at room temperature. These compounds should be stable for at least 3 weeks (*11*). DOPA was stored at 5 °C and 1,2-dihydroxybenzene at room temperature, and both were used within 3 days. An aqueous solution of KIO_4 (500 mL, 2.00×10^{-2} M) was transferred into an amber container and stored in the dark when not in use.

Table I. Determination of 1,2-Diols via Lead Periodate Formation

compound	μmol taken	μmol found	recovery, %	RSD[a]
1,2-ethanediol	2.00	1.94	97.0	± 2.6% (8)
1,2-propanediol	2.00	1.84	93.0	± 6.1% (7)
1,2-dihydroxybenzene	2.00	1.97	98.5	± 5.6% (9)
1-amino-2,3-propanediol	2.99	2.93	98.1	± 5.5% (7)
1-phenyl-1,2-ethanediol	0.886	0.916	103.4	± 14% (8)
1,2-ethanediol	0.40	0.37	93	± 14.5% (8)
DL-β-3,4-dihydroxyphenyl alanine	0.40	0.41	102	± 11.5% (10)

[a] Figures in parentheses indicate the number of determinations.

The periodate concentration was checked iodimetrically by titrating the unreacted arsenite (*2*). KIO_4 was chosen as the oxidant because the concentration needed was low, its solution has an aqueous pH of 5.1 which is closer to neutrality, and the effect of overoxidation is minimized (*13*, *14*). A 500-mL stock solution of $Pb(NO_3)_2$ containing 1000 μg Pb/mL was prepared with 1 M HNO_3. Standard solutions were then prepared by appropriate aliquot dilution from the stock solution to provide standards in the 150 to 230 μg Pb/mL range. In all the aqueous solution preparations and subsequent precipitate washings, deionized and permanganate-distilled water was used (*15*).

Procedure. To a 15-cm test tube containing 1.00–2.30 mL of the diol sample in water, 1.00 mL of 2.00×10^{-2} M KIO_4 was added, mixed well and left standing for 2–5 min. The concentration of the diol was 0.40–4.00 μmol/mL. (In a separate experiment, where the reaction mixture was conducted in the dark and in ambient laboratory light, no detectable difference in absorbance measurements was noticed.) One mL of 4×10^{-2} M $Pb(NO_3)_2$ was added to the reaction mixture and the solution was mixed for approximately 30 s to precipitate the lead periodate. This solution must not be left standing for more than 2 min as lead periodate in aqueous solution adsorbs onto the test tube. The contents of the test tube was poured into a disposable filtration unit and suction was applied. The test tube was rinsed 3 times with approximately 6-mL portions of deionized and distilled water. The filtrate was then decanted through the suction vent under reduced pressure. The filtering and decanting processes were repeated twice with 20 mL of deionized and distilled water. Care must be taken to mix the filtrate each time before decanting to prevent localized concentration of any excess $Pb(NO_3)_2$ reagent. After the last decantation, 10.00 mL of 1 M HNO_3 were distributed onto the membrane filter and allowed to remain standing for 30 s before suction was applied. This digestion step was repeated twice. The 30 mL of dissolved lead ion were poured out through the disconnected suction vent into a stoppered flask. The sample was ready for atomic absorption analysis.

A blank was required and its preparation incorporated all steps described above except the addition of diol. The difference in absorbance between the blank and the sample is proportional to the concentration of diol.

RESULTS AND DISCUSSION

Results have been presented for six aliphatic and aromatic diols in Table I. The error increases by about twofold at the lowest concentration level, 0.40 μg/mL. Tables II and III contained results of analysis in admixture or in the presence of simulated impurities, respectively. The useful range of analysis is 1.5–4.0 μg/mL for which the relative deviation is 2.6–6.9%. Since the analyses were conducted at room temperature using mild reagent concentrations and neutral solutions, selectivity was maintained and overoxidation avoided. The average recovery is 98.5% with a rapid analysis time of 15 samples/h.

Limit of Concentration Range and Effect of Filter Porosity. The upper limit was affected by the solubility of $Pb(IO_3)_2$ in water, which is 30 mg/L at 25 °C (*16*). This corresponds to 3.9 μmol/mL diol for the volume of reaction mixture encountered. In a separate experiment, solutions of $Pb(NO_3)_2$ and KIO_3 were mixed, and the precipitate was observed when the concentration of $Pb(IO_3)_2$ was greater than 4 μmol/mL. It was possible to increase the upper limit when the volume of the solution mixture was increased but this was not further investigated. Medium (10–15 μm) and fine (4–5.5 μm) fritted Pyrex glass filters were examined, and visual loss of precipitate was observed in the former, while filtering in the latter was slow, even under suction. When a filtration unit (4.5-cm diameter and 0.2-μm porosity) was used under suction, the filtration rate was fast and no loss of precipitate was noted.

Table II. Determination of Mixtures of 1,2-Diols

		μmol each diol taken	total μmol diol taken	total μmol diol found	recovery, %	RSD[a]
mixture 1	1,2-ethanediol	1.00	2.00	1.87	93.3	±6.9% (7)
	1,2-propanediol	1.00				
mixture 2	1,2-dihydroxybenzene	2.00	3.80	3.85	101.3	±6.2% (8)
	DOPA[b]	1.80				
mixture 3	DOPA	1.80	3.58	3.51	98.0	±5.5% (8)
	1-phenyl-1,2-ethanediol	0.886				
	1-amino-2,3-propanediol	0.897				

[a] Figures in parentheses indicate the number of determinations. [b] DOPA = DL-β-3,4-dihydroxyphenylalanine.

Table III. Determination of 1,2-Diols in the Presence of Simulated Impurities

compound	simulated impurities[b]	μmol taken	μmol found	recovery, %	RSD[a]
1,2-ethanediol	methanol ethanol 2-propanol 1-butanol formaldehyde formic acid	2.00	2.04	102.1	± 4.7% (8)
1,2-propanediol		2.00	2.08	103.9	± 6.0% (8)
DL-β-3,4-dihydroxyphenylalanine	1,3-dihydroxybenzene 1,3,5-trihydroxybenzene	1.52	1.48	97.2	± 6.0% (6)

[a] Figures in parentheses indicate the number of determinations. [b] In the presence of 2 μmol of each of the impuriti

Table IV. Solubilities of Metallic Iodates and Periodates

	silver (I)[a]	lead (II)[a]	mercury (II)[a]	copper (II)[a]	iron (III)[a]
periodate[b]	dark brown precipitate	white precipitate	brown precipitate	green precipitate	clear brown solution
treated with nitric acid[c]	precipitate partially dissolved	solution became clear	precipitate partially dissolved	clear blue solution	clear brown solution
iodate[b]	white precipitate	clear solution	white precipitate	clear blue solution	clear brown solution
treated with nitric acid[c]	precipitate remained	clear solution	solution became clear	clear blue solution	clear brown solution

[a] 1 mL of 1 M metallic nitrate was used. [b] 1 mL of 2×10^{-3} M of KIO_3 or KIO_4 was used. [c] Up to 0.1 mL of concentrated HNO_3 solution was added.

Other Metallic Periodates. Several other metallic periodates were also considered for use. These periodates are characteristically known for their different valencies (*13*, *17*). Lead periodate has been identified as the triplumbous paraperiodate, $Pb_3H_4(IO_6)_2$ (*18*) and therefore, the lead to iodine ratio is 3:2. In Table IV, the solubilities of various metallic iodates were compared to those of the corresponding periodates. Their relative solubilities in concentrated HNO_3 were also investigated. It was not possible to precipitate silver periodate since its iodate coprecipitated under these conditions. Iron periodate and iodate precipitate did not form. The mercury periodate was separated from its iodate only if concentrated HNO_3 was added, but the mercury periodate was also partially dissolved. These metallic compounds were not used because they could not give analytical separation of periodate and iodate. It is possible, however, to use either lead or copper reagent. Copper reagent was not investigated but it should be possible to extend the analytical range as the solubility of $Cu(IO_3)_2$ is 1.36 g/L at 15 °C (*19*), and thereby improve the analysis precision.

Types of Diols and Impurities. The effect of the presence of amino, amino acid, and non-adjacent dihydroxy or trihydroxy side chains was tested for the periodate oxidation. Though these groups are known to undergo periodate oxidation (*2*), the reactions are too slow to be regarded as satisfactory for analysis. Glycine, 1,3-dihydroxybenzene and 1,3,5-trihydroxybenzene were only slightly oxidized (ca. 0.05 μmol/mL), under the same experimental conditions. The significant difference in the reaction rates makes it possible for 1-amino-2,3-propanediol and DOPA to be determined successfully. Methanol, ethanol, isopropanol, *n*-butanol, formaldehyde, and formic acid were all similarly tested for oxidation and negligible oxidation was found. This is of particular significance as ethanol and 1,3-dihydroxybenzene could be impurities present in 1,2-ethanediol and DOPA, respectively. Furthermore, the negligible oxidation of HCHO and HCOOH (which are common periodate oxidation products) provides selectivity to diol analysis. No significant interference was observed in the presence of up to 2.0 μmol/mL of each of these simulated impurities (Table III). Mixtures of diols were also analyzed. The analysis yielded the total concentration of the diols but individual diols were indistinguishable.

Interference. The periodate reaction was attempted on 1,2,3-propanetriol and 1,2,3-trihydroxybenzene but the reaction was slow and only approximately 50% of the expected oxidation occurred. Therefore, adjacent 1,2,3-trihydroxy compounds will interfere with diol determination if present. A solution of 1,4-dihydroxybenzene is unstable, oxidizes in air, and interferes in the periodate reaction (*20*). 1,2-Dihydroxybenzene interacts with 1,3-dihydroxybenzene and 1,3,5-trihydroxybenzene in aqueous solution, as evidenced from the different coloration of mixtures. In all these considerations, spurious results were obtained when samples were analyzed.

CONCLUSION

The application of IAAS to the determination of 1,2-diols has significant advantages in terms of analysis speed and specificity, but with poorer precision. The detection limits are compatible with existing methods. This procedure may be modified to include analysis of other selective functional groups known to undergo periodate oxidation (*11*). Preliminary experiments have indicated that styrene glycol can be determined in the presence of styrene epoxide. This is of particular interest because epoxide hydrase catalyzes the hydrolysis of an epoxide to a 1,2-diol. The procedure may lend itself to the determination of the enzyme activity of epoxide hydrase, known for its pivotal role in the metabolism of many carcinogens and toxic compounds.

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